

December 4, 2003

Ken Zweibel
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12

Dear Ken:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period October 03, 2003 to November 03, 2003, under the subject subcontract. The report highlights progress and results obtained under Task 3 (Si-based Solar Cells) and Task 4 (Diagnostics).

Task 3: Si-based Solar Cells

Si Film Growth

Post-deposition annealing experiments of Al/Si bi-layers were carried out during this period to compare crystallization and layer inversion processes in standard metal induced crystallization and in-situ metal induced crystallization. The use of evaporated Si films also allows comparison between films deposited in an H free environment and HWCVD films. First, 0.5 μm thick films of Al were deposited onto 7059 glass substrates by electron beam evaporation. The films were left in ambient air for a period of 24 hours to allow formation of an oxide layer. Although the role of the oxide layer is not well understood, literature reports indicate its presence is required to achieve layer inversion and a continuous polycrystalline Si film. Si films with 0.6 μm thickness were then deposited by electron beam evaporation and HWCVD. XRD measurements showed no evidence of crystallization of the Si films deposited by evaporation prior to annealing (Figure 1). On the other hand, XRD and Raman data indicated complete crystallization of the films deposited by HWCVD (Figure 2). Figure 3 is an optical micrograph through the glass substrate of the sample deposited by HWCVD. In this picture, the bright regions represent Al while the

dark regions are Si grains at the glass interface. These reflectivity observations have been corroborated by Raman spectroscopy. Figure 3 clearly shows that a continuous Si film was not obtained at the end of deposition. The films deposited by HWCVD were thus added to the annealing set to find if further layer inversion could be achieved. Annealing of all films was performed in a tube furnace for 90 min at 500°C under 100 sccm of Ar. For the samples with Si films deposited by evaporation, optical microscopy showed polycrystalline Si nucleation extending to the glass interface (Figure 4). However for the annealing time and temperature used, there was very little lateral grain growth. Consistent with this observation, XRD analysis showed only partial crystallization of these films (Figure 1). For samples with Si films deposited by HWCVD, no increase in grain coalescence or crystalline fraction was observed. All of these samples were further annealed at the same conditions, for an additional 5 hrs. However, no change in properties were observed after annealing.

Doping Si Films

Previously, results were reported on boron doping experiments of HWCVD films. The films were deposited at 500 mTorr and 450°C with B_2H_6/SiH_4 flow ratios varying from 10^{-5} to 10^{-3} . For all dopant gas concentrations, the resulting dark conductivity of the films were 10^{-6} S/cm. In order to understand whether the invariance in conductivity was the result of the deposition conditions or film structure, additional doped films were deposited. Deposition conditions and film properties for this sample set are given in Table 1, which also includes one sample (HW217-21) from the previous experimental set. Comparison of samples HW223-11 and HW217-21 clearly indicates that the deposition pressure does not play a role in affecting the film conductivity. For sub-micron films, the conductivity changes 3 orders of magnitude by changing the B_2H_6/SiH_4 from 10^{-3} to 10^{-2} , as seen between samples HW226-11 and HW217-21. Furthermore, if the film thickness is increased by a factor of 3 while keeping other conditions constant (see samples HW226-11 and HW227-11), the conductivity increases another 2 orders of magnitude. The fact that the activation energy of both of these samples is the same indicates an increase in mobility with thickness. The reasons for this dependence are not clear, however, a possible explanation is the existence of a highly defective or amorphous incubation layer in the initial stages of growth.

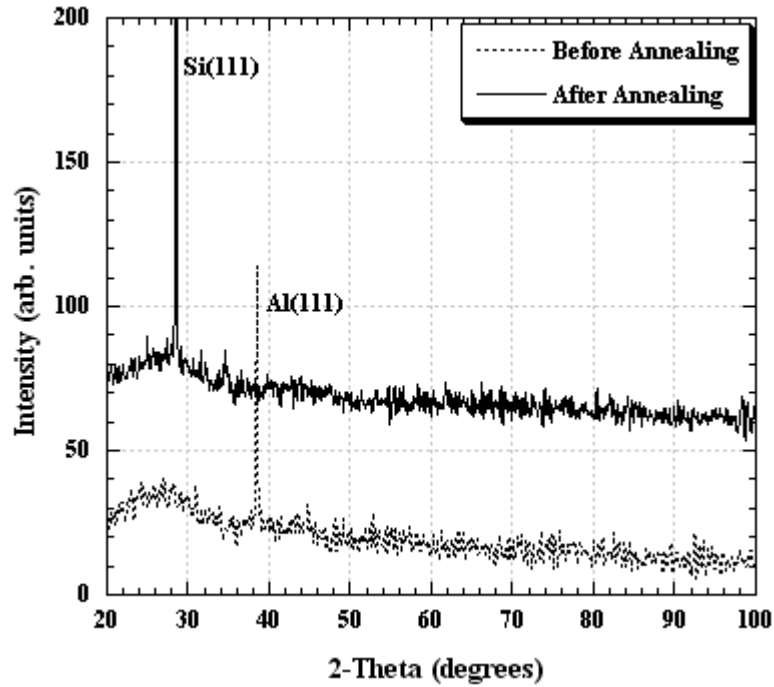


Figure 1. XRD pattern of evaporated Si film on Al before and after annealing.

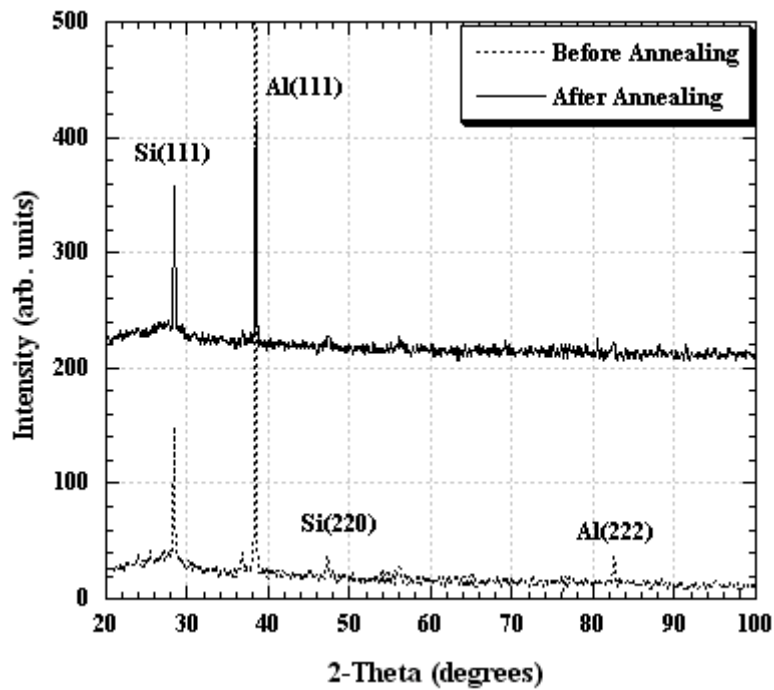


Figure 2. XRD pattern of HWCVD Si film on Al before and after post deposition annealing.

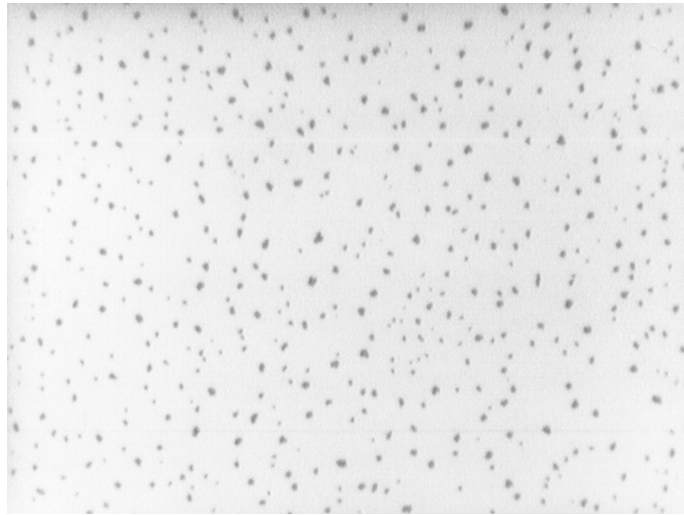


Figure 3. Optical micrograph through the glass substrate of Si film deposited by HWCVD.

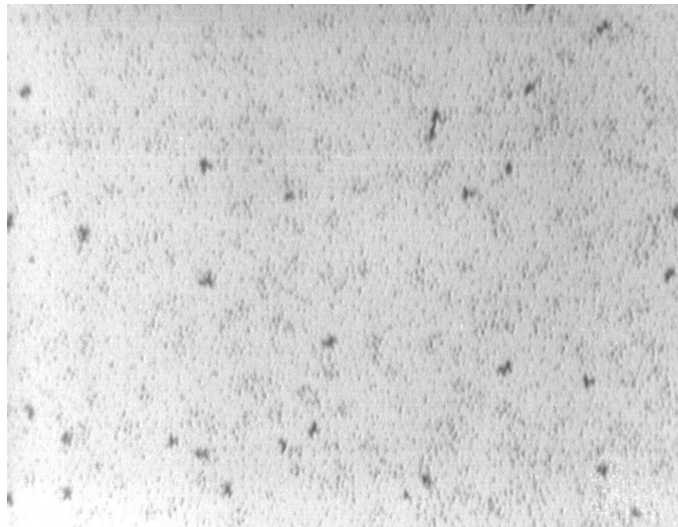


Figure 4. Optical micrograph through the glass substrate of Si film deposited by evaporation after 90 min anneal at 500 °C.

Table 1. Deposition conditions and film properties of B-doped Si films.

Sample #	Thickness (nm)	Deposition Conditions	Conductivity (S/cm)	Activation Energy (eV)*
HW217-21	0.5	P=200 mTorr B ₂ H ₆ /SiH ₄ = 1.0x10 ⁻³ F _{SiH₄} = 4 sccm T _f = 1850 °C T _s = 450 °C Gr = 1.0 nm/hr	Dark=1.1E-6 Photo=same	Not Measured
HW223-11	1.5	P=500 mTorr B ₂ H ₆ /SiH ₄ = 1.0x10 ⁻³ F _{SiH₄} = 4 sccm T _f = 1850 °C T _s = 450 °C Gr = 3.0 nm/hr	Dark=1.0E-6 Photo=same	0.088
HW226-11	0.8	P=200 mTorr B ₂ H ₆ /SiH ₄ = 1.0x10 ⁻² F _{SiH₄} = 3 sccm T _f = 1850 °C T _s = 450 °C Gr = 1.2 nm/hr	Dark=1.5E-3 Photo=same	0.041
HW227-11	2.5	P=200 mTorr B ₂ H ₆ /SiH ₄ = 1.0x10 ⁻² F _{SiH₄} = 3 sccm T _f = 1850 °C T _s = 450 °C Gr = 1.2 nm/hr	Dark=1.1E-1 Photo=same	0.040

***all films had curved Arrhenius plots over 213 to 373K, Ea from fit only 213-293 K**

Additional films were deposited in the thickness range of 30-50 nm in order to develop doped films for window layers. Preliminary results show that all films have conductivities of 10⁻² S/cm for B₂H₆/SiH₄ flow ratios of 0, 1x10⁻² and 4x10⁻². The invariance in conductivity between undoped and doped films at these dopant gas concentrations probably reflects a dominating effect of the film surface on the conductivity values. This effect has been reported by other groups for films in this thickness range. For future work, doped films in the range of 200 nm thickness will be deposited to study the bulk properties of films adequate for window layers. In regards to the study of impurities incorporation in PECVD and HWCVD films, a set of representative samples deposited before and after different contaminant burying runs has been sent to NREL for SIMS characterization. Results of this analysis will be reported in the next period.

Task 4: Diagnostics

Contact Wetting Angle Measurements

During this contract period, the measurement apparatus was upgraded by the addition of a CCD camera and software, enabling digital acquisition of drop profiles after application, thereby allowing many drops to be systematically sampled for later analysis. For each applied drop, the left and right side contact angles were measured from the CCD images on the surface of CdTe and CIGS thin films. The application of a droplet on a solid surface was accomplished by using a simple bulb dropper placed at a fixed height of about 2cm above a thin film sample. A single droplet was placed on the surface of the sample and allowed to stand for at least 10 seconds to allow the droplet to reach equilibrium with the solid surface, and a digital image of the droplet on the thin film was captured. The temperature is also measured and is maintained at $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Figure 5 displays a typical digital image of the right and left contact angles of a liquid droplet on a solid surface.

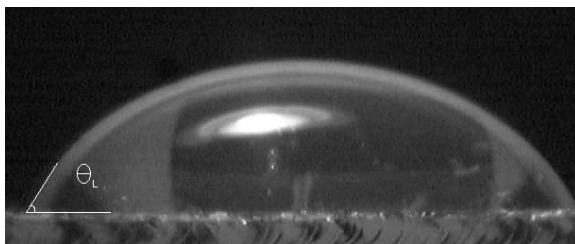


Figure 5. Digital microscopic image of deionized water on a CdTe surface.

Image analysis software, such as Pixelpoint freeware, is used in conjunction with the digital picture so that the magnitude of the right and left contact angles for each droplet could be determined. The angular data was imported to a spreadsheet for analysis and archiving; the average value of the left and right contact wetting angles of each droplet was used to represent the characteristic contact angle for that particular drop for that particular liquid. The average of the six characteristic contact angles for each droplet represented the overall contact angle for the fluid that had been used. This value was used with the overall contact angle for a different fluid and the energy equations given in the report for July, 2003 were solved simultaneously to determine the polar and dispersive components of the surface energies of CIGS and CdTe films.

CIGS

CIGS films with up to 8.5% Ga were analyzed with two liquid combinations: water-formamide and water-acetophenone. Preliminary results indicate that the gallium composition reduces surface energy slightly, from 72 dyne/cm at 0% Ga to 65 dyne/cm at 8.5% Ga. The dispersive components of the surface energy of CIGS remained essentially constant, but above 6% Ga, the polar component decreased, suggesting that increasing the Ga concentration changes the surface

configuration. Further investigation will employ samples over a broader compositional range and GIXRD and XPS measurements to obtain a detailed analysis of the surface condition with increasing Ga composition.

CdTe

The contact wetting angles of a sample of physical vapor deposited (PVD) CdTe films were measured immediately following deposition and at various times thereafter. The CdTe samples were stored: 1) in a vacuum dessicator at 100 mTorr; 2) in a “dry” dessicator at a constant relative humidity level of 35%; and 3) in an enclosed vessel with water. Full analysis of the surface energies has not been completed, and XPS and GIXRD analysis will be conducted on these samples to determine the surface composition and to determine if a correlation exists that relates changes in contact wetting angles to changes in oxidation on the surface of the CdTe thin film.

Sincerely,

Robert W. Birkmire
Director

RWB/bj

Cc: Gerri Hobbs
Cc: Carolyn Lopez
Cc: Roger Aparicio
Cc: Steven Hegedus
Cc: Brian McCandless